Phosphors Preapred by RF-Sputtering Technique

Akiyoshi Mikami and Kazushi Yamamoto
Kanazawa Institute of Technology, Electrical Engineering
Ohgigaoka 7-1, Nonoichi, Ishikawa 921-8501, Japan
Tel:+081-76-248-9642, Fax:+081-76-294-6711, E-mail:mikami@neptune.kanazawa-it.ac.jp

Abstract

A new phosphor MgS:Eu has been studied as a candidate for the pure red emission in thin-film electroluminescent(EL) devices. It was observed that the EL device shows typically reddish orange emission with the peak wavelength of 595nm and CIE color coordinates of (0.536, 0.453). The luminance(L_{40}) of 300cd/m^2 at 40V above the threshold voltage(160V) was obtained by 1-kHz pulse voltage excitation. In order to improve the color purity, we tried to make a ternary $Mg_{1-x}Ca_xS$:Eu phosphor by employing a co-sputtering technique. As is expected, the wavelength of the emission band significantly shifts to the longer wavelength side by the small amount of Ca composition. Only 10～20% of Ca replacing Mg is enough to satisfy the color purity of the CRT red phosphor. The device exhibits a pure red emission having a peak wavelength of 630nm and CIE coordinates of (0.663,0.332) in the $Mg_{0.8}Ca_{0.2}S$:Eu phosphor. In addition, the response speed was confirmed to be several micro-seconds, which is in contrast to slow behavior in the CaS:Eu phosphor. The possibility of the pure red emission for the filter-less display will be discussed in the presentation.

Technical Summary

[1] Background and Objective

In the past several years, inorganic EL displays do not make a significant progress for lack of color capability. Only the monochrome orange emitting EL devices are widely used in the market of test-and-measurements, industrial-control, medical, and transportation because of the high reliability. Recently, the other display products such as "Multicolor EL" and transparent "Automobile EL" have been commercialized and become a subject of research activities with the help of large size hybrid EL display and new efficient blue phosphor.

About five years ago, A.Mikami and co-workers[1)] proposed a new phosphor structure consisting of $Zn_{1-x}Mg_xS$:Mn and ZnS:Mn stacked layers, which clearly realized an improved color coordinates and luminance of the filtered green and red components, because of the energy shift of the Mn emission peak originating from the Mg incorporation in ZnS. In these systems, the red component is filtered from the orange-yellow emission of the ZnS:Mn, which is unfortunately only the red phosphor for the practical application. The last year, ZnS:Mn,LiF was further proposed for the improved filtered red emission by our group[2)]. However, new red phosphor without taking color filters will be required for the further progress.

In this paper, we first demonstrate MgS:Eu thin-film phosphor as a candidate for the red-emitting EL device. It is well known that the CaS:Eu exhibits the pure red emission[3)], but the research activity has been reduced because of the inefficient deep red emission with a peak wavelength of 660nm, and its slow response characteristics in the emission and charge density due to the time-dependent carrier injection process[4)]. Relatively high luminance will be reported in this work. In addition, color control was successfully attempted by a partial replacement of Mg^{2+} ions with Ca^{2+} ions. The luminescent characteristics have been investigated in detail in terms of growth conditions, annealing temperature and Ca composition.

[2] Experimental Results

2.1 Sample preparation

Figure 1 shows a schematic structure of the device consisting of the red phosphor layer sandwiched by very high breakdown-voltage Zr_xSi_yN insulating layers developed by our laboratory. Thin-film MgS:Eu phosphors were fabricated by means of rf-magnetron sputtering system with a 4-inch diagonal cathode. Typical sputtering conditions are as follows. The argon gas was used as an atmosphere, in which the pressure is optimized in the range between 1×10^{-1} and 5×10^{-1} pa. and rf-power was supplied between 100 and 200W. A MgS(99.999%) powder source was synthesized by high temperature heat treatment for the purpose of outgas and re-crystallization followed by mixing with EuS(99.99%) powders. The composition of Ca in $Mg_{1-x}Ca_xS$:Eu phosphor was varied in the range up to 20% by employing thin CaS tablets located on the MgS powder target. The deposited films were annealed at typically 600°C for one hour in vacuum.

photoluminescence(PL). The Eu concentration was kept constant at 0.2mol% throughout the experiments. In the MgS host, the Eu^{2+} ion exhibits the emission peak around 595nm in EL, and a little bit lower peak energy (~600nm) in PL. The CIE color coordinates of EL is (0.536, 0.453), which visually appears to be reddish orange color. Figure 3 shows typical luminance and luminous efficiency as a function of applied voltage in the MgS:Eu thin-film EL device when is driven by 1-kHz pulse excitation . The luminance rapidly rises around a threshold voltage(V_{th}) of 165V, and attains approximately 300cd/m^2(L_{40}) at 40V above V_{th} . The maximum efficiency(η_{max}) is about 0.45-lm/W, although the strict optimization of the growth conditions has not yet been done. These characteristics are superior to that of CaS:Eu thin-film EL devices in which the previous paper reported a luminance(L_{40}) of 200cd/m^2 and a maximum efficiency of 0.05-lm/W(η_{max}), respectively[3].

The small incorporation of Ca^{2+} ions into the MgS compound was found to be very effective for the improvement of color purity in the emission of Eu^{2+} ions. Figure 4 shows the variation of CIE color coordinates of Eu emission in the $Mg_{1-x}Ca_xS$:Eu phosphors with the Ca content range up to 0.2. It is surprising that the only 5% of Ca^{2+} ions drastically improves the color purity of the Eu emission. In the case of x=0.1, the color coordinates are comparable to the CRT red phosphor(Y_2O_2S:Eu). When the Ca composition is further increased to 20%, sufficient red emission can be realized with (x=0.663, y=0.332). The color coordinates of the emission are also summarized in Table 1. The CaS:Eu phosphor showed the color coordinates of (0.692, 0.306) in our laboratory, which is too deep to realize the practical visual efficiency. In our experiments, the MgS thin-film has a cubic structure with preferred orientation of (100) plane in the similar manner to CaS. Since the ionic radius of the Eu^{2+} ion is relatively close to the Ca^{2+} ion rather than the Mg^{2+} ion, the Eu^{2+} ion will be selectively substituted into the Ca site, resulting in the large energy shift in the crystal field theory.

We try to measure the response characteristics of the MgS based thin-film EL devices, because it is well known that the CaS:Eu thin-film has a serious problem in the response characteristics of the emission due to the time-dependent injection and trapping process of charge carriers in the CaS host. Fortunately, the MgS:Eu device has almost the same response speed as the conventional ZnS:Mn thin-film EL device. The emission intensity rapidly rises within a time of pulse width, and attains a saturated value in a few pulses. In conclusion, the emission color of the Eu center is significantly affected by the neighboring Ca^{2+} ions, but the electrical characteristics are not so affected as long as the Ca composition is at least less than 20%. The detail luminescent characteristics of the $Mg_{0.8}Ca_{0.2}S$:Eu thin-film EL device will be discussed in the presentation.

[3] Original Aspects and Impact

Although the high luminance green phosphor and the pure blue-emitting phosphor have been already developed in the field of inorganic EL devices, the pure and highly efficient red-emitting material is missing. It is a consensus of opinion that the matter of CaS:Eu and ZnS:Sm phosphors still remains unsolved. Only orange-yellow emission from ZnS:Mn phosphor is used as a red component of color EL displays with color filter. In this work, we found that the MgS:Eu thin-film EL device has a relatively high efficiency and high response speed, compared with CaS:Eu. In addition, pure red emission can be easily obtained by small amount of Ca incorporation without scarifying the response characteristics. It is emphasized that this paper presents a new red component for the filter-less structure such as transparent display and bright full-color EL display.

[4] References

(1) A.Mikami, I.Washizuka, "A 14.4-in. diagonal high contrast multicolor information display", Int.Display Workshop(IDW'97), Nagoya, p.601(1997). / IEICE Trans. on Electronics, E81-C, No.11, p1725 (1998).

(2) A.Mikami, K.Yamamoto, "Effect of LiF doping on the color shift in ZnS:Mn,LiF red emitting EL devices", Int.. Display Workshop(IDW'01), Nagoya, p1135. (2001).

(3) K.Tanaka, A.Mikami, et.al "High brightness red electroluminescence in CaS:Eu thin films", Appl. Phys. Lett. 48, No.25 p.1730 (1986).

(4) M.Ando, Y.A.Ono, "Role of Eu centers in electrical-optical characteristics of red-emitting CaS:Eu thin-film EL devices", App.Phys.Lett. 68, No.7, p.3578 (1990).

[5] Previous publications

This paper has completely original results, which is not presented and published anywhere. The last year, we presented a new reddish orange emitting ZnS:Mn,LiF phosphor, which has an efficient red components in comparison with the conventional ZnS:Mn. The present paper gives the solution of the remained problem on the pure and filter-less red-emitting phosphor for the first time.

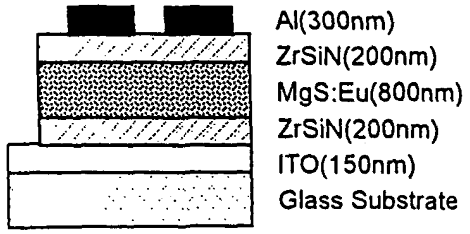

Fig.1 Schematic structure of the red light- emitting thin-film EL device with MgS:Eu or $Mg_{1-x}Ca_xS$:Eu phosphor layer used in this experiment.

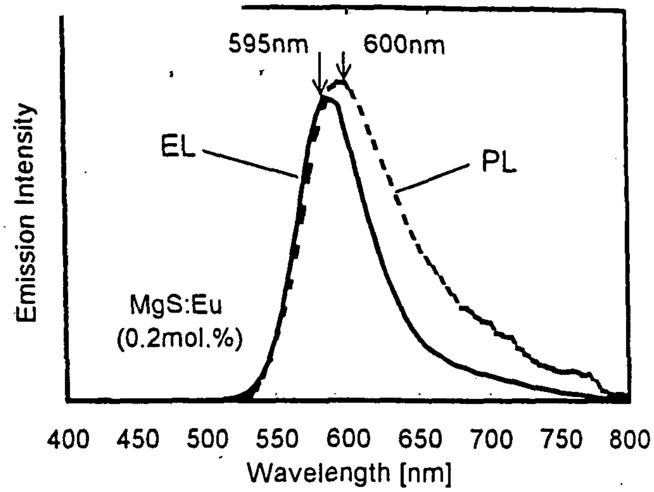

Fig.2 Elecroluminescence(EL) and photoluminescence(PL) in MgS:Eu thin film phosphor deposited on the ZrSiN insulating layer by rf-sputtering method. The sample was excited by mono-chromed 460nm-Xe light in PL measurement.

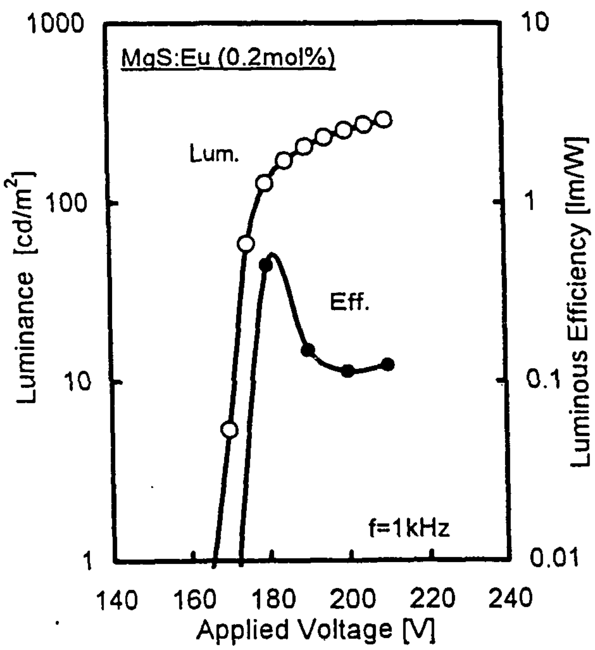

Fig.3 Typical luminescence and luminous efficiency as a function of applied voltage in the MgS:Eu thin-film EL device.

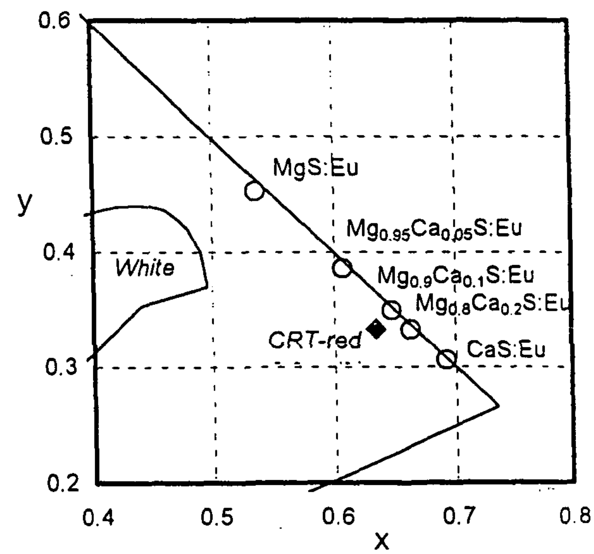

Fig.4 CIE diagram showing the color coordinates of the MgS:Eu and $Mg_{1-x}Ca_xS$:Eu phosphors as a function of composition range up to 0.2. The data of CaS:Eu and CRT-red point were also shown in comparison.

Table 1 CIE color coordinates of the MgS:Eu and $Mg_{1-x}Ca_xS$:Eu and CaS:Eu phosphors studied in this work.

Phosphor	CIE-x	CIE-y
MgS:Eu	0.536	0.453
$Mg_{0.95}Ca_{0.05}S$:Eu	0.607	0.386
$Mg_{0.9}Ca_{0.1}S$:Eu	0.644	0.350
$Mg_{0.8}Ca_{0.2}S$:Eu	0.663	0.332
CaS:Eu	0.692	0.306